MO 4: Femtosekundenspektroskopie II

Zeit: Montag 16:30–19:00 Raum: 3G

MO 4.1 Mo 16:30 3G

Monitoring Electron Tunneling Dynamics in Molecules with Attosecond Precision — •Stefanie Graefe and Misha Yu. Ivanov — Steacie Insitute for Molecular Sciences, National Research Council Canada, Canada

Recent experiments have demonstrated control of electron localization during strong-field induced ionization and subsequent dissociation of molecular deuterium (D_2) (Kling et al., Science 2006). As the molecular ion D_2^+ created after strong-field ionization vibrates, the returning electron excites the molecular ion into the dissociative σ_u state. Recollision and excitation of the σ_u state occur in the presence of the strong laser field, which creates a coherent superposition of the σ_u and σ_g states. This superposition corresponds to an electron localized on one of the two protons, breaking the symmetry in molecular dissociation.

To observe electronic dynamics, the spectroscopic techniques have to be on the same time-scale as the dynamics to be observed - the attosecond time-scale. Although attosecond pulses are spectrally very broad (several eV), we demonstrate that information about electronic tunneling motion can be extracted by monitoring asymmetries in the time-resolved photoelectron distribution. A theoretical description for calculating time-resolved spectra in the presence of a strong laser field is given. Taking the electronic localization dynamics as an example, it is demonstrated that electron tunneling can be observed by interferences in the photoelectron spectra, based on a mechanism similar to interfering pathways in coherent control (double-slit setup).

MO 4.2 Mo 16:45 3G

Manipulation von Femtosekundenimpulsen im Mittelinfraroten - Schwingungsenergieübertragung in Nitrophenylalanin — •Karin Haiser, Florian Koller, Markus Huber, Nadja Regner, Wolfgang Schreier, Tobias Schrader und Wolfgang Zinth — Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, 80538 München

Eine Voraussetzung für die zweidimensionale Infrarotspektroskopie sind spektral schmalbandige und abstimmbare ultrakurze Anregungsimpulse im mittleren Infraroten. Diese Impulse können durch Differenzfrequenzmischung (DFM) von zwei fs-Nahinfrarotimpulsen erzeugt werden. Spektrale Einschränkung erreicht man dadurch, dass den Nahinfrarotimpulsen vor der DFM ein definierter und einstellbarer Chirp aufgeprägt wird. So lassen sich bandbreitebegrenzte schmalbandige Mittelinfrarotimpulse (Dauer ca. 1 ps) erzeugen. Zusätzlich ist eine schnelle, computeransteuerbare Abstimmung der spektralen Lage in einem Bereich von 200 cm^{-1} möglich.

Für ein Anreg-Abtast-Experiment im Mittelinfraroten wurden diese Anregungsimpulse zur Untersuchung der Übertragung von Schwingungsenergie an der Aminosäure Nitrophenylalanin eingesetzt. Dabei wurden verschiedene Schwingungsmoden einzelner Molekülgruppen gezielt angeregt und deren Wechselwirkung untereinander systematisch untersucht. Es konnten Kopplungsmechanismen verschiedener Art beobachtet und teilweise intramolekularen Energierelaxationsprozessen zugeordnet werden.

MO 4.3 Mo 17:00 3G

Molecular sensing with a fibre laser using interferometric nonlinear vibrational spectroscopy — •Bernhard von Vacano, Jean Rehbinder, Tiago Buckup, and Marcus Motzkus — Physikalische Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany

Compact fs-fibre lasers promise to make nonlinear spectroscopy available for real-life applications. In a simple scheme, we demonstrate nonlinear vibrational spectroscopy with a single beam of femtosecond pulses from an unamplified fibre laser oscillator. To achieve high spectral resolution and sensitive signal detection with only picojoule pulse energies available, pulse shaping and integrated interferometric detection is employed. The spectroscopic technique used is coherent anti-Stokes Raman scattering (CARS), obtaining well-resolved spectra of molecular vibrations of halomethane samples in the liquid phase, covering 100 - 350cm^{-1}. We explore the implications of phase control for the interferometric detection of weak signals. The presented combination of fiber laser, pulse shaping and CARS microspectroscopy is a first example of simplified schemes for compact and robust nonlinear spectroscopic detection and sensing, which is demonstrated exemplarily by online monitoring the chemical composition in a microfludic flow cell.

MO 4.4 Mo 17:15 3G

Femtosecond Dynamics of Phenylcarbenes — •Bastian Noller[1], Ingo Fischer[1], Lionel Poisson[2], and Jean-Michel Mestdagh[2] — [1]Institut für Physikalische Chemie, Universität Würzburg, Deutschland — [2]Laboratoire Francis Perrin, CEA Saclay, France

Carbenes play an important role in combustion chemistry and interstellar space and have gained considerable interest in synthesis over the last years. The electronic states of carbenes often have very small energy gaps between each other and are of considerable interest as a "benchmark"for improving quantum mechanical methods. The photophysics of carbenes is not well investigated due to the experimental challenge. The dynamics of several phenylcarbenes (*Ph-C-R*), with a variety of substituents (i.e. $R{=}CH_3$, CF_3, *Cl*), were investigated by femtosecond time-resolved pump probe spectroscopy in a free jet. REMPI spectra were recorded with a nanosecond laser setup. The carbenes were produced by jet flash pyrolysis of diazirines. Time-of-flight mass spectrometry, photoion- and photoelectron imaging were employed as detection methods in the femtosecond time-resolved experiments. The excited state dynamics depended on the substituents (R) and will be compared to models based on qualitative excited state calculations. Preliminary results indicate that conical intersections along the rotation coordinate of the group R against the phenyl ring and/or along the coordinate of a 1,2-H-shift in the excited state play an important roles for state deactivation.

MO 4.5 Mo 17:30 3G

Femtosecond Dynamics of Electron Transfer in a Neutral Organic Mixed-Valence Compound — •Markus Margraf[1], Juliane Köhler[1], Raman Maksimenka[1,2], Alexander Heckmann[1], Christoph Lambert[1], and Ingo Fischer[1] — [1]University of Würzburg, Department of Chemistry, 97074 Würzburg — [2]Laboratoire Francis Perrin, CEA Saclay, F-91191 Gif-sur-Yvette Cedex

A neutral organic mixed valence compound was studied by femtosecond time-resolved transient absorption spectroscopy with the aim to gain insight into its charge-transfer dynamics upon optical excitation. The back electron transfer was investigated in five different solvents: n-hexane, toluene, dibutyl ether, methyl-tert-butyl ether (MTBE) and benzonitrile. In the pump step, the molecule was excited at 760 nm and 850 nm into the intervalence charge-transfer band. The resulting transients can be described by two time-constants. We assign one time-constant to the rearrangement of solvent molecules in the charge transfer state and the second time-constant to back-electron transfer to the electronic ground state. On the one hand we investigated the influence of the solvent polarity on the rate of back electron transfer, on the other hand the dependence on orientation of polarisation between pump- and probepulse. Back electron transfer rates range from $1.5 \cdot 10^{12} s^{-1}$ in benzonitrile through $8 \cdot 10^{11} s^{-1}$ in MTBE, around $1.6 \cdot 10^{11} s^{-1}$ in dibutylether and toluene and to $3.8 \cdot 10^{9} s^{-1}$ in n-hexane.

MO 4.6 Mo 17:45 3G

Determination of electronic transition dipole moment orientations by polarization re-solved femtosecond VIS-pump / IR-probe spectroscopy — Martin Linke, Moritz Theisen, Alexandra Lauer, Henk Fidder, and •Karsten Heyne — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany

Excitation of an isotropic ensemble of molecules with linear polarized light pulses leads to an anisotropic distribution of excited molecules (photoselection). During anisotropy decay conformational changes and the orientation of transition dipole moments can be identified by femtosecond polarization resolved pump-probe experiments. We determined the orientations of electronic and infrared transition dipole moments of Coumarin 314 and of Chlorophyll a molecules in solution.

The orientation of the electronic transition dipole moment of the Qy band within the molecular structure of Chlorophyll a is the basis for simulating many properties of photosynthetic systems. Determinations thus far of the electronic transition dipole moment orientations of Chlorophyll a were made on oriented samples with steady state spectroscopy, and with steady state anisotropy experiments. These experiments yielded angles for the orientation of the Qy electronic transition dipole moment with respect to the x-axis varying from 70° to 90°. Using polarization resolved VIS pump / IR-probe experiments we reinvestigated this issue.

MO 4.7 Mo 18:00 3G

Ultrafast Singlet versus Triplet Dynamics in Thin Pentacene Films — •Henning Marciniak[1], Stefan Lochbrunner[1], and Bert Nickel[2] — [1]Intstitut für Physik, Universität Rostock — [2]Fakultät für Physik und CeNS, LMU München

Thin pentacene films are frequently applied as active layers in prototypical organic electronic devices. Their electronic structure and dynamics determine to a large extent the device behavior. We investigate with femtosecond absorption spectroscopy microcrystalline pentacene films with a thickness of roughly 30 monolayers. The transient spectra show that optically excited singlet excitons decay within 70 fs to a non fluorescing species [1]. The fission of a singlet exciton into two triplet excitons is discussed as potential relaxation path. The process was observed in crystalline tetracene and the time scale is feasible since the total spin is conserved. By tilting the pentacene layers relative to the incident laser beams it is possible to probe singlets and triplets or exclusively singlets since the transition dipole of the lowest triplet-triplet absorption band is orientated along the long axis of the upstanding molecules. A transient absorption band at 525 nm can thereby be identified as triplet absorption. However, it rises with a time constant of about 0.9 ps instead of 70 fs and it is more than a factor of 10 weaker than expected. We conclude that triplet formation is a secondary step and only a small fraction of excitons experiences fission into triplets. The majority transforms probably to excimer excitons.

[1] H. Marciniak, M. Fiebig, M. Huth, S. Schiefer, B. Nickel, F. Selmaier, and S. Lochbrunner, Phys. Rev. Lett. **99** (2007), 176402.

MO 4.8 Mo 18:15 3G

Heterogeneous Electron Transfer Dynamics in Systematically Varied Perylene/TiO2 Systems — •Antje Neubauer, Jodi Szarko, Andreas Bartelt, Rainer Eichberger, Olaf Lettau, and Carlo Fasting — Hahn-Meitner-Institut, Berlin

We present fs-transient absorption measurements of perylene dyes attached to TiO2 colloidal films in ultrahigh vacuum and compare the photoinduced electron injection and recombination dynamics.

New perylene derivatives with a systematic structural change were synthesized and chemically bound to nano-structured colloidal anatase films via a carboxylic anchor group. Extending the distance between the aromatic rings of the perylene and the carboxylic anchor group starting with one double bond and going up to five double bonds also changed the photophysical properties of the dyes.

Prior to the fs-transient absorption experiments, the electronic states of the dyes in solution and bound to the TiO2 surface were studied with steady-state absorption and fluorescence spectroscopy. In all these experiments, a systematic red shift of ground, cationic, and excited state absorption bands were observed with increasing chain length.

Electron injection rates were below 30 fs, with the exception of an additional longer component in the range of 120 fs for the perylene dye with the longest chain. At the same time, the recombination process slowed down significantly with increasing chain lengths. The data suggest strong electronic coupling in the case of electron injection and weaker coupling for electron recombination.

MO 4.9 Mo 18:30 3G

Rotational diffusion measured by optical transient anisotropy — •Oliver Schalk and Andreas-Neil Unterreiner — Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, 76128 Karlsruhe

Rotational diffusion in real time can be observed by transient anisotropy, which is often interpreted in terms of correlation functions. However, anisotropy is sensitive to the transition dipole moment (i.e., only 2 dimensions are to be considered) which leads to a modified decay mechanism. To consider anisotropy explicitly, a new ansatz is shown where rotational diffusion is described by a step model that is able to interpolate between free rotation and media with high viscosities. For collision-free reorientation, a different initial decay and long-time behavior is obtained and compared to models based on correlation functions – however, the new ansatz describes the experiments more satisfactorily. The behavior of collisional anisotropy decay has been modeled by means of Monte-Carlo simulations allowing for a variation of angular correlation and energy transfer. As shown, this approach is easily extendable to multiphoton processes.

MO 4.10 Mo 18:45 3G

Ultrafast Electronic and Vibrational Spectroscopy of LOV1C57S Mutant — •Alexander Weigel and Luis Perez Lustres — Institute for Chemistry, Brook-Taylor-Str. 2, 12489 Berlin

The photoactivation of Phot proteins involves two LOV-domains binding flavin mononucleotide as a chromophore. We utilized femtosecond transient absorption spectroscopy to identify the earliest events succeeding the excitation of the C57S mutant of *Chlamydomonas reinhardtii* LOV1 domain. In accordance with literature the excitated S_1 state was found to decay with a lifetime of ∼2 ns accompanied by a rise of the triplet state spectrum. Several additional features were observed on the shorter timescale. Directly after excitation spectral hole burning reveals the vibrational structure of the transient spectra. Rearrangement of the active site and intramolecular vibrational redistribution lead to a subsequent broadening with time constants of 100 fs and 1 ps. The time traces show pronounced oscillatory behaviour, at least six frequencies between 41 cm^{-1} and 420 cm^{-1} could be extracted. Two types of oscillations may be distinguished. One part bears a varying phase over the spectral bands and is clearly attributed to vibrational wavepacket motion. The rest exhibits constant phase behaviour and could stem from vibronic coupling to a $n\pi^*$ state in the vicinity of S_1. In accordance with this model an evolution with a time constant of 190 ps and a similar spectral distribution is observed. It is intended to use femtosecond stimulated resonance Raman spectroscopy to further clarify the origin of the oscillations and gain additional insight into structural rearrangements. Preliminary results are presented.